

PRODUCTION AND APPLICATION OF THIOSULFATE IN LIME-BASED WET FGD

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INTRODUCTION

Thiosulfate has been identified as a free radical scavenger which inhibits sulfite oxidation effectively (Owens and Rochelle, 1985). In flue gas scrubbers, excessive oxidation could cause some serious reliability problems such as scaling on scrubber internals and mist eliminators. Emulsified sulfur has been used in many limestone scrubbers (Moser et al., 1988) since it was found that sulfur could react with sulfite in scrubbing liquor to form thiosulfate feasibly (Rochelle et al., 1987). However, the reaction rate is very slow primarily because of the low solubility of sulfur in aqueous solution. Alkaline hydrolysis of sulfur is a potential alternative to synthesize thiosulfate by sulfur addition. At high pH and high temperature, sulfur can be converted to thiosulfate and polysulfides which react with sulfite readily to form thiosulfate. This paper is focused on the kinetics of the alkaline hydrolysis of sulfur and its effect on the overall performance of lime-based wet FGD.

BACKGROUND

Several reactions related to the production of thiosulfate from sulfur are collectively listed in Table 1. Thiosulfate has been produced commercially by the reaction of sulfur and sulfite in neutral or alkaline media (rxn 1). Because of the equilibrium between sulfite and bisulfite (rxn 2), alkalinity is necessary to enhance reaction 1 by removing the proton released from bisulfite. The reaction rate is independent of pH or sulfite concentration and is first order in sulfur solids concentration when pH is above 5.0 and sulfite is greater than 1 mM (Donaldson and Johnston, 1969). At 55°C, typical for lime/limestone slurry scrubbers and recycle tanks, 0.04 hr⁻¹ was suggested for this first order kinetic constant (Rochelle et al., 1987).

One way to facilitate the production of thiosulfate is by using sulfide or polysulfides instead of sulfur (rxn 4). Polysulfides may be formed by dissolving sulfur in sulfide solutions (Gould, 1962). Reaction 4 is so fast that the proton released by reaction 2, in some instances, cannot be neutralized immediately. Besides, the pH at gas-liquid interface is low due to SO₂ dissolution. The consequence is the formation of "local" low pH spot despite the alkaline bulk solution and the generation of hydrogen sulfide that may cause serious odor problems. Because of this reason, polysulfide was abandoned in the EPA limestone scrubbing pilot plant at Research Triangle Park (Rochelle et al., 1987). However, if polysulfides are introduced to scrubbers together with lime slurries, the high pH of the feeding slurry and the scrubbing liquor as well as the fast dissolution of lime will neutralize the proton in reaction 2 effectively and therefore prevent the formation of H₂S.

Boiling sulfur-lime slurry is a commercial process for polysulfide production.

Alkaline hydrolysis of sulfur is therefore a logical approach to synthesize thiosulfate in situ because of the highly exothermic reaction of lime slaking. The polysulfides will react readily with sulfite to form thiosulfates (rxn 7-9). The unreacted sulfur leaving the lime slurry storage tank will react with sulfite in the scrubbers and in the recycle tanks to produce additional thiosulfate (rxn 1). Another "reactor" for thiosulfate production is the thickener. Therefore, the conversion of sulfur to thiosulfate is expected to be substantially higher in lime-based FGD than in limestone-based FGD.

EXPERIMENTAL METHODS

Jacketed reactors were used to perform experiments at the desired temperature. The solutions were agitated by magnetic stirrers. When thiosulfate formation in slakers/lime tanks was studied, 500 ml of 3.3 wt% or 10 wt% lime slurry was used to react with sulfur. The slurry samples (25 ml) were quenched by adding 50 ml cold 0.2M sodium sulfite. The resulting mixtures were allowed to react 10 minutes to completely convert polysulfides to thiosulfate. Clarified filtrates were then analyzed for thiosulfate by iodometric titration after blocking sulfite with formaldehyde. The thiosulfate measured in this way was dubbed "available thiosulfate."

When the formation of thiosulfate by reacting sulfur with sulfite was studied, a calcium sulfite slurry available from a power station's (Elrama, PA) recycle tank was used as the source of sulfite. Fritted glass spargers were used to introduce gas containing SO_2 to the reacting solutions. Lime slurries (10 wt%) were used to neutralize the absorbed SO_2 and to keep the pH between 6.5 and 7.5. Both emulsified sulfur and powdered sulfur were used for this study. Emulsified sulfur had no problem getting into slurry solution while 2000X dilute Triton X-100 was needed to wet powdered sulfur first.

A schematic diagram of the flow system used for studying the impact of sulfur addition to a lime slurry scrubbing system is given in Figure 1. Nitrogen, air, and SO_2 were metered and mixed in a mixing chamber to simulate the flue gas. In most cases, both nitrogen and air were set at 1.0 scfm to give ~10% O_2 in the simulated flue gas. Sulfur dioxide was set at a rate slightly lower than necessary to neutralize the 5 wt% lime slurry fed at 12 ml/min. An auxiliary SO_2 flow was activated by a pH controller when the pH value of the scrubbing liquor was higher than 7.2. The scrubber pH was thus maintained between 7.0 and 7.2 throughout all experiments. The temperature of the scrubbing liquor was maintained at 55°C by circulating the liquor through a heat exchanger. The simulated thickener overflow (TOF) was fed to the scrubber at 100 ml/min. The composition of the simulated TOF is also given in Figure 1. Sodium thiosulfate or available thiosulfate was fed to the scrubber at 16 ml/min. The volume of the absorber was maintained at 5.5 liters by a level controller. Samples were taken once an hour and analyzed for both sulfite and thiosulfate by iodometric titration.

RESULTS AND DISCUSSIONS

Sulfur to Thiosulfate and Polysulfides in Slakers and Lime Tanks

Boiling a slurry mixture of lime and sulfur is a general practice to

manufacture polysulfides commercially. This process prompted the testing of thiosulfate production by feeding sulfur to the slaker or the lime slurry storage tank because of the fast conversion of polysulfides to thiosulfate and the highly exothermic reaction of lime slaking. According to the reactions 6-9 listed in Table I, one mole of sulfur will generate one mole of thiosulfate stoichiometrically. The calculation of sulfur conversion is based on the formation of the available thiosulfate.

Both powdered sulfur and emulsified sulfur were tested for the production of available thiosulfate. It is very clear that the conversions of powdered sulfur (Figure 2) and emulsified sulfur (Figure 3) to available thiosulfate are strongly dependent on reaction temperature. The dramatic difference between 70°C and 80°C in converting powdered sulfur to available thiosulfate is probably not exclusively due to the activation energy of reaction 6. A possible contribution is the dissolution of powdered sulfur in sulfide or polysulfide solutions. As a matter of fact, one way to produce polysulfide is dissolving powdered sulfur in sodium sulfide solution (Hartler et al., 1967; Arntson et al., 1958). Therefore, when the concentration of sulfide or polysulfide is high, the conversion of sulfur to available thiosulfate will be accelerated. The ceiling conversion is probably controlled by the thermodynamic equilibrium and the coprecipitation with lime solids.

Figure 2 indicates that higher concentrations (1.0 g S/500 ml lime slurry) of sulfur are subjected to lower conversion rates. Probably the agglomeration of sulfur particles, that reduces the available surface area for reactions, is more severe at higher concentrations. Emulsified sulfur is a lot more reactive than powdered sulfur for alkaline hydrolysis. Compared to powdered sulfur (>30 μ), emulsified sulfur (<5 μ) is at least 100 times more reactive at 70°C primarily due to its smaller particle size.

It is well known that thiosulfate is not stable in acidic solution (rxn 3). It is also known that thiosulfate decomposes to sulfate and sulfide in alkaline media (Kirk-Othmer, 1969). To investigate the stability of thiosulfate in lime slurry, sodium thiosulfate was added to 3.3 wt.% lime slurry. The samples at different "seasoning" time were analyzed for thiosulfate. The results indicate that 20% and 30% of the sodium thiosulfate are not accounted for in the filtrate for 12.5 mM and 25 mM sodium thiosulfite solutions respectively, however the thiosulfate concentrations did not change with time. Another study, mixing lime slurry (3.3 and 10 wt%) with varying amounts of sodium thiosulfate (up to 25.3 mM) for one hour at 80°C, indicated that the unaccounted for fraction was larger when using more concentrated lime slurry. These results imply that the major source of unaccounted thiosulfate is the "coprecipitation" with lime, while the decomposition of thiosulfate in lime saturated solutions is probably not significant. This was verified by analyzing the available thiosulfate in the filtered lime solids. Nevertheless, thiosulfate incorporation into lime solids should not cause any problems in lime slurry scrubbing systems because as the lime dissolves the coprecipitated "available thiosulfate" will be released.

Sulfur to Thiosulfate in Scrubbers and Recycle Tanks

Scrubbers and recycle tanks are the major reactors for the conversion of sulfur to thiosulfate (rxn 1) in limestone slurry scrubbing systems. For lime slurry scrubbing systems, the unreacted sulfur leaving from lime slurry storage tank

will contribute additional thiosulfate generation in scrubbers and recycle tanks. The reaction rate can be expressed empirically as first order in sulfur solids concentration (eq. 10)

$$\frac{d[S]}{dt} = -k[S] \quad (10)$$

Based on reaction 1 and equation 10, equation 11 can be derived.

$$\ln \left(1 - \frac{[S_2O_3]_t - [S_2O_3]_0}{[S]_0} \right) = -kt \quad (11)$$

Where subscripts t and o denote time t and time zero respectively. Plotting the experimental data as $\ln \left(1 - ([S_2O_3]_t - [S_2O_3]_0) / [S]_0 \right)$ versus time should then give a straight line of slope -k. The results are summarized in Table 2.

The conversion of sulfur to thiosulfate by reacting with sulfite decreased with increasing sulfur loading just like what was observed in the study of alkaline hydrolysis of sulfur. When sulfur solid concentration increased from 0.4 g to 1.2 g per 500 ml slurry, the empirical reaction rate constant decreased from 0.072 hr⁻¹ to 0.040 hr⁻¹ when N₂ blanket was applied above the reaction solutions. Similar results were reported by Rochelle et al. (1987). However, no significant differences were observed with different sulfur loadings (0.17-1.2 g) when gases were sparged through the solutions. Probably, the gas sparging helps the dispersion of sulfur solids and enhances the solid-liquid reactions.

In reacting with sulfite to form thiosulfate, emulsified sulfur has significantly larger initial conversion rate while powdered sulfur has an "incubation" period. The latter was also observed by Rochelle et al. (1987). The reaction rate constant measured after incubation period is 0.087 hr⁻¹ for powdered sulfur. The corresponding kinetic constant for emulsified sulfur is 0.090 hr⁻¹. In other words, there is no significant difference between emulsified sulfur and powdered sulfur except for the much faster initial rates of emulsified sulfur and the long incubation time of powdered sulfur.

Previous studies suggested a kinetic constant of 0.04 hr⁻¹ at 55°C in the absence of sulfite oxidation (Rochelle et al., 1987). Thiosulfate decomposition is coupled with sulfite oxidation. Table 2 indicates that the kinetic constants are well above that value even in the presence of significant sulfite oxidation caused by 15% O₂. Perhaps some unidentified chemistry facilitated the conversion of sulfur to thiosulfate in Elrama slurries more effectively.

Impact of Available Thiosulfate on the Performance of Wet Scrubber

In a laboratory scale slaker, elemental sulfur (32 g powdered sulfur or 45.7 g 70 wt% emulsified sulfur was mixed with 10 liter preheated water (46°C) first and 2 kg pebble lime was then fed to the water-sulfur mixture. The slurry temperature rose and then dropped from 81.5°C to 72°C over 25 minutes. The slurry was then diluted with water make 8.4 wt% solids. The temperature was maintained at 44°C by a heating tape and the slurry was gently stirred for one hour. The slurry was then quenched with water to make 5.0 wt% slurry. The conversions of sulfur to available thiosulfate were 78% and 21% for emulsified sulfur and powdered sulfur, respectively.

A bench scale absorber was used to evaluate the effect of the available thiosulfate on the general performance of magnesium-enhanced lime slurry scrubber. During the experiments, lime slurry and available thiosulfate were fed to the absorber separately. Separate feeding made the control of thiosulfate concentration independent of the lime slurry feed rate. A very light odor of emulsified sulfur was detected during the process of conducting experiments, but no H_2S odor problem was encountered.

The result indicated that the oxidation of sulfite could be suppressed by thiosulfate when thiosulfate concentration was higher than a certain level, the so-called threshold concentration. For example, 0.63 mM thiosulfate gave a calcium sulfite/sulfate solid with 87% oxidation, which was essentially the same as the solid oxidation in the absence of thiosulfate. As low as 15% solid oxidation was achieved when 1.8 mM thiosulfate was present.

Two experiments were performed under similar conditions except one used $Na_2S_2O_3$ directly and the other used polysulfides, which were produced by alkaline hydrolysis of sulfur, as the source of thiosulfate. The results show practically no difference between these two experiments except polysulfides slightly decreased calcium and increased sulfate but kept the oxidation level in the solids (15%) essentially the same.

It seemed that polysulfides reacted with sulfite fast enough to provide thiosulfate reliably. Fortunately, the absorption of SO_2 into lime slurry to supply sulfite for thiosulfate production was even faster. Therefore, the concentration of sulfite in the solution was maintained nearly constant. Sulfite is important because SO_3^{2-} is the major source of alkalinity used to absorb SO_2 .

Figure 4 shows the effect of thiosulfate concentration on its utilization. The utilization here is defined as the ratio of the measured thiosulfate concentration to the "maximal" thiosulfate concentration, which is obtained by assuming no decomposition and no coprecipitation. The results imply that the major loss of thiosulfate is due to coprecipitation with calcium sulfite hemihydrate when thiosulfate concentration is higher than 1.9 mM. (Because thiosulfate utilization in the absence of oxygen is 92%, which is not significantly higher than 85-88% utilization with 1.9-3.8 mM thiosulfate in the scrubbing liquor and 10.5% O_2 in the flue gas. And the thiosulfate degradation is supposed to be coupled with sulfite oxidation). Thiosulfate utilization increases with its concentration up to 1.9 mM thiosulfate. This trend implies that thiosulfate, at lower concentration, is subjected to more severe chemical degradation. It seems consistent with previous study (Maller et al. 1988), which correlated thiosulfate degradation rate (R_{deg}) and sulfite oxidation rate (R_{ox}) as:

$$R_{deg} = a(R_{ox} \times [S_2O_3^{2-}])^{0.5} \quad (12)$$

$$R_{ox} = b([SO_3^{2-}]/[S_2O_3^{2-}]) \quad (13)$$

Equations (12) and (13) can be combined to give equation (14):

$$R_{deg} = c[SO_3^{2-}]^{0.5} \quad (14)$$

Where a , b , and c are constants. In other words, the degradation of thiosulfate was predicted to be half order in sulfite but was independent of thiosulfate concentration. Equation (15) can be derived from equation (14) if the sulfite concentration is maintained constant:

$$\frac{[S_2O_3^{2-}]}{[S_2O_3^{2-}]_0} = 1 - \frac{[SO_3^{2-}]^{0.5}}{d[S_2O_3^{2-}]_0} \quad (15)$$

Where d is a constant. Equation (15) indicates qualitatively that the utilization of thiosulfate increases with thiosulfate and decreases with sulfite. More research is needed to better understand the degradation and coprecipitation of thiosulfate in lime slurry scrubbing systems.

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TABLE I
THIOSULFATE FORMATIONS IN LIME SLURRY SCRUBBING SYSTEMS

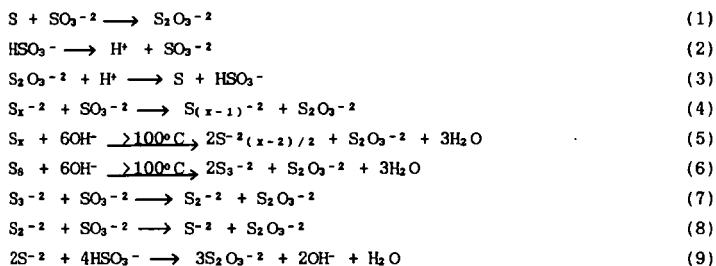


TABLE 2
SUMMARY OF KINETIC CONSTANTS OF THIOSULFATE
FORMATION BY REACTING SULFUR WITH SULFITE AT 55°C

Sulfur (powdered) (g/500 ml slurry)	Reaction Rate Constant (hour ⁻¹)		
	N ₂ Blanket	1% SO ₂ 200 ml/min	2000 ppm SO ₂ 15% O ₂ 1 l/min
0.1668		0.081	0.042
0.336		0.087	0.049
		0.090*	0.052
0.40	0.072	0.059	
1.20	0.040	0.062	

*0.4766 g 70 wt% emulsified sulfur

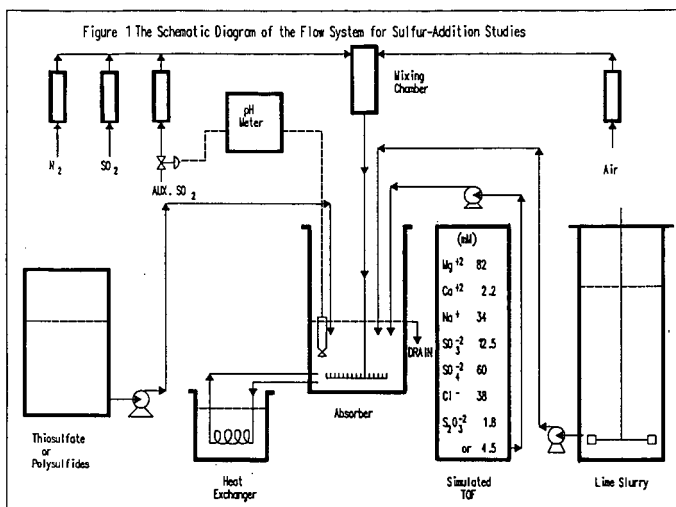


Figure 2 Temperature Effects on Alkaline Hydrolysis of Sulfur

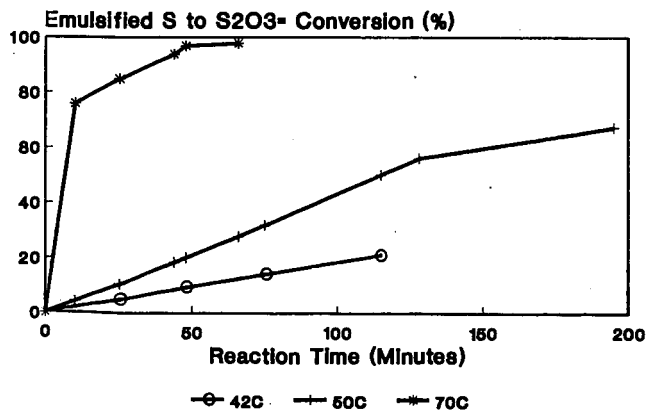


Figure 3 Temperature and Sulfur Loading Effects on Alkaline Hydrolysis of Sulfur

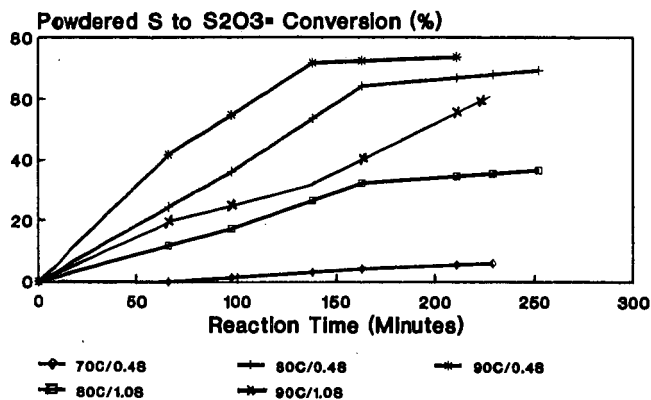


Figure 4 Utilization of Thiosulfate in Thiosorbic Lime Slurry Scrubbers

